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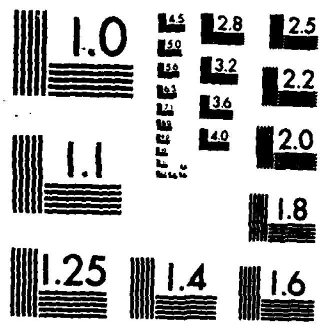

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Vibrational Excitation of an Adbond by a Short-Pulsed Laser

by

Sander van Smaalen and Thomas F. George

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VIBRATIONAL EXCITATION OF AN ADBOND BY A SHORT-PULSED LASER

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ABSTRACT

A system of a phonon-damped adbond, coherently excited by a laser, is considered. The effect of a series of laser pulses is compared with the effect of a continuous-wave laser.

INTRODUCTION

Consider an adsorbed atom in a vibrational bond, driven by a laser, and damped due to the lattice vibrations of the substrate. We approximate the vibrating adatom by a one-dimensional oscillator, for the motion pependicular to the surface.

The interaction between the adatom and the substrate is given by the potential between the atom and the nearest surface atom. Choose the origin on the average position of the surface atom . Let z be the position of the adatom and denote the z-component of the displacement of the surface atom by u_z. Then the problem can be separated in a vibration of the adatom in the potential $V(z-z_0)$, and the interaction with the lattice vibrations, in first order given by

$$H_{ap} = -u_z \frac{dV(z-z_0)}{dz}. \tag{1}$$

A master equation for the time evolution of the reduced density operator of the adbond is then[1-3]

$$\frac{d\sigma(t)}{dt} = \frac{1}{i\hbar} [H_a, \sigma(t)] - \Gamma \sigma(t), \tag{2}$$

where Γ is the Liouville relaxation operator. Using that the adbond potential is strongly anharmonic then leads to a set of equations for the level populations $\sigma_n(t)$,[1-3]

$$\frac{d\sigma_n(t)}{dt} = \sum_k \{a_{kn} \sigma_k(t) - a_{nk} \sigma_n(t)\}. \tag{3}$$

Expressions for the transition rate constants a_{kn} can be found in refs. 1-3.

PULSED-LASER EXCITATION

The laser couples the two levels $|g\rangle$ and $|e\rangle$ of the adbond. Then

the interaction of the ad-bond with the laser is given by,

$$H_{ar}(t) = \Omega(t) \{|e\rangle\langle g| \exp(-i\omega t) + |g\rangle\langle e| \exp(i\omega t)\} \qquad (4)$$

where $\Omega(t) = -\vec{\mu}.\vec{E}_0(t)/\hbar$ is the Rabi frequency, $\vec{\mu} = \langle g|\vec{\mu}|e\rangle$ is the transition dipole moment, and $\vec{E}(t) = \vec{E}_0(t) \cos(\omega t)$ is the electric field of the laser beam. For a cw laser $\vec{E}_0(t)$ is independent of time. For a pulsed laser we assume that $\vec{E}_0(t)$ is slowly varying compared with the laser frequency ω.

An expression for the time evolution of the reduced density operator when the laser is present is obtained by adding $H_{ar}(t)$ to H_a in Eq.2. It is easily seen that the master equation (Eq.3) then also involves the coherences of σ between $|g\rangle$ and $|e\rangle$.

Assume the pulse duration Δt to be much shorter than the inverse of the rate constants in Eq.3. Then the relaxation can be neglected during the pulse, and the effect of the pulse is found from the equations for a two-level system. On resonance it depends only on the pulse area :

$$\theta = \int_{pulse} dt\, \Omega(t) \qquad (5)$$

The solution is

$$\begin{aligned} R_2(\Delta t) &= R_2^0 \cos(\theta) + R_3^0 \sin(\theta), \\ R_3(\Delta t) &= R_3^0 \cos(\theta) - R_2^0 \sin(\theta), \end{aligned} \qquad (6)$$

where $R_3 = \sigma_e - \sigma_g$ is the population inversion, and $R_2 = i(\tilde{\sigma}_{eg} - \tilde{\sigma}_{ge})$ is the imaginary part of the coherence in the rotating frame.

A series of equally-spaced π-pulses ($\theta = \pi$) is considered. From Eq.6 it follows that the effect of a π-pulse is to change R_3^0 into $-R_3^0$. If we assume that $R_2^0 = 0$, then it remains zero throughout. Between the pulses (occurring at intervals t_p), the adbond evolves in time according to the master equation (Eq.3). After several pulses the system will reach a quasi steady state in which the time evolution of $\sigma(t)$ is identical in each interval t_p. Then we can express the populations entirely in the rate constants a_{kn} and the time t_p.[4]

COMPARISON WITH CW LASER EXCITATION

An adbond, irradiated by a cw laser, reaches a steady state in which the populations are independent of time. The steady-state values, $\sigma_n(\infty)$, are obtained by solving the master equation for

$d\bar{\sigma}(t)/dt = 0$. The result is given in table I. For the pulsed laser, with the adbond in the quasi steady state, an average value for the populations can be defined as

$$\sigma_n(av) = \frac{1}{t_p}\int_0^{t_p} dt\ \sigma_n(t). \tag{7}$$

It is then possible to compare the average "exciting power" of the pulsed laser with that of the cw laser by calculating $\eta = \sigma_e(av)/\sigma_e(\infty)$, and using some criterion to compare both laser.

The first criterion is to require that both lasers have the same average power. In the low-intensity limit, $\Omega_{cw} \ll \gamma$, we find $\eta \ll 1$, that is, the cw laser is much more effective in exciting the adbond then the pulsed laser. In the high-intensity limit $\sigma(\infty)$ and $\sigma(av)$ aquire the same limiting values, and $\eta = 1$.

The second criterion is to require that the average power absorption from the laser is equal in both cases. It follows that $\eta = 1$, independent of the laser power. Conversely, this expresses the fact that the energy flow into the substrate is proportional to the excitation of the adbond and does not depend on the details of this excitation.

Table I Comparison of a cw laser and a pulsed laser

	continuous wave laser	pulsed laser
average laser power	Ω^2_{cw}	$\frac{\pi^2}{\Delta t\ t_p}$
average absorbed power	$\hbar\omega \frac{\Omega^2_{cw}}{\gamma}(\sigma_g - \sigma_e)$	$\hbar\omega \frac{1}{t_p} R_3(\Delta t)$
average excited-level population	$\sigma_e(\infty) = \frac{\Omega^2_{cw}}{\gamma^2 + 2\Omega^2_{cw}}$	$\sigma_e(av) = \frac{(1 - \exp[-\gamma t_p])}{t_p(1 + \exp[-\gamma t_p])}$

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